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㊿発明の名称　半導体基板の洗浄装置

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発明の名称

半導体基板の洗浄装置

特許請求の範囲

アンモニア（$NH_4OH$）または塩酸（$HCl$）または硝酸（$HNO_3$）の蒸気を発生する蒸気発生部と、前記蒸気発生部より発生した蒸気中にオゾン（$O_3$）ガスを導入するガス導入部とを具備することを特徴とする半導体基板の洗浄装置。

発明の詳細な説明

〔産業上の利用分野〕

本発明は半導体基板の洗浄装置に関する。

〔従来の技術〕

従来、この種の洗浄装置としては、半導体基板を洗浄液の中に浸漬し処理を行なうディップ式と呼ばれる洗浄装置が主流となっていた。また、回転させた半導体基板に霧状にした洗浄液を噴き付けるスプレー式や、洗浄液をスピン塗布させるスピン式の洗浄装置も用いられていた。

〔発明が解決しようとする課題〕

しかしながら、上述した従来のディップ式洗浄装置では、半導体基板を直接洗浄液に浸漬し処理するため、洗浄液中に不純物の微粒子が存在すると、この微粒子が半導体基板表面に付　するという問題がある。そのため、処理槽内の洗浄中の微粒子を除去するための循環沪過装置が不可欠であるが、この循環沪過装置によっても微粒子の付着を完全には防ぐことができず、連続処理を行なうと洗浄液中に微粒子が蓄積する。また、洗浄液が何らかの原因によって汚染された場合、その汚染された洗浄液で処理された半導体基板が全て汚染される。

一方、スプレー式やスピン式洗浄装置では、洗浄液を1バッチ毎に使い捨てにして使用しているため、微粒子の蓄積による半導体表面への再付着は少ないという利点はあるものの、やはり洗浄液が直接半導体基板に触れているために、洗浄液が

汚染された場合には処理された半導体基板が汚染されることは、ディップ式の場合と同じである。

洗浄工程で半導体基板表面に付 した微粒子や汚染物質は、それに続く半導体製造工程、即ち拡散・酸化，リソグラフィ等の各工程において悪影響を及ぼす．例えば、拡散・酸化工程においては異常拡散の原因となったり、酸化膜厚が不均一になったり、結晶欠陥を誘起する原因となったりする．また、リソグラフィ工程ではパターン欠陥の原因となったりする．このため、半導体素子の特性を劣化させ、歩留りの低下，品質の低下を招くという問題がある．

従来のスプレー式あるいはスピン式洗浄装置では洗浄液を使い捨てにしているため、ディップ式の場合と比較して薬品の使用量が増えるという問題もある．

さらに、従来のディップ式，スプレー式およびスピン式洗浄装置では、酸化剤として過酸化水素を用いているが、洗浄液中の過酸化水素の分解によって洗浄液が劣化し、洗浄能力も長時間持続しないという問題がある．また、過酸化水素の分解によって生ずる気泡のため、洗浄液が細部にまで行き渡らないという問題がある．特に、近年半導体素子の集積度が増すにつれて、アスペクト比が増加する傾向にあり、高アスペクト比でも確実に洗浄できることが要求されてきている．

洗浄液の劣化を防ぐために、過酸化水素の代わりにオゾン（$O_3$）ガスを用いる方法もあるが、従来の洗浄装置では洗浄液中に$O_3$をバブリングによって供給しているため、洗浄効果が不均一になりやすいという問題もあった．

〔課題を解決するための手段〕

本発明の半導体基板の洗浄装置は、アンモニアまたは塩酸または硝酸の蒸気を発生する蒸気発生部と、この発生した蒸気中にオゾンガスを導入するガス導入部とを具備するものである．

〔実施例〕

次に、本発明について図面を参照して説明する．

第1図は本発明の第1の実施例を示す洗浄装置の模式断面図である．

第1図において、処理槽1の底部に、例えばアンモニア（又は、塩酸あるいは硝酸）溶液2が供給されている．このアンモニア溶液2をヒーター3で加熱することによってアンモニア蒸気を発生させる．この場合、蒸気発生部4はヒーター3によって構成されている．発生されたアンモニア蒸気中にオゾン・ガスがオゾン・ガス導入管5によって導入される．オゾンはオゾン発生器6に供給された酸素（$O_2$）ガスの一部がオゾン発生器6でオゾン化され、オゾン／酸素（$O_3/O_2$）の混合ガスとして、フィルター7を通して導入される．この場合、ガス導入部8は、オゾン発生器6，フィルター7およびオゾン・ガス導入管5から構成される．

このようにしてオゾン・ガスが導入されたアンモニア蒸気中に半導体基板9が晒され処理される．半導体基板9はキャリア10によって保持されている．アンモニア蒸気は冷却器11によって液化された後処理槽に戻され再利用される．

このように本実施例においては、アンモニアを蒸気として利用することにより、元の薬品中に微粒子や汚染物質が存在していたとしても、半導体基板表面への付着を防止することができ、また細部まで均一に洗浄することができる．

本第1の実施例では加熱に投げ込み式のヒーターを使用しているが、処理槽外部から加熱する方式を用いてもよく、また赤外線加熱，ランプ加熱等による加熱方式を用いることも可能である．また、本第1の実施例ではアンモニアを用いた場合について説明したが、塩酸や硝酸を用いても全く同様に半導体基板を洗浄することができる．

第2図は本発明の第2の実施例を示す洗浄装置の模式断面図である．

本第2の実施例においては、アンモニア蒸気は水蒸気にアンモニア・ガスを接触させることによって得ている．硝酸，塩酸蒸気は、二酸化窒素，塩化水素ガスを用いる．水蒸気発生器21で作られた水蒸気は蒸気発生器22に送られる．蒸気発生器22において、アンモニア・ガス（$NH_3$）

供給置23よりフィルター7Aを通して供給されてきたアンモニア・ガスは水蒸気に吸収され、アンモニア蒸気が生成する。生成されたアンモニア蒸気は処理槽1に導入される。

処理槽1内には、酸素ガス供給装置24からフィルター7Bを通して酸素ガスが同時に導入される。この時、処理槽1の側面に設置された紫外線光源25より紫外線が照射される。この紫外線の働きによって酸素ガスがオゾン化される。こうして、アンモニア蒸気とオゾンとの混合雰囲気中で半導体基板9が処理される。本第2実施例の場合においても半導体基板9はキャリア10に保持されているが、枚葉処理ももちろん可能である。

第3図は、本実施例および従来のディップ式洗浄装置を用いた場合の、半導体基板表面に付着する微粒子の測定結果である。

半導体基板を従来の装置と本実施例により10分間処理した後、純水により10分間リンスを行ない、乾燥後に半導体基板表面に付着していた微粒子を計測した。従来の装置で処理した場合、$HCl/H_2O_2/H_2O$, $HNO_3/H_2O_2$ では微粒子数は1枚当たり100個程度であり、$NH_4OH/H_2O_2/H_2O$では20個程度であった。これに対して本実施例の洗浄装置で処理した場合、いずれの場合においても微粒子数は1枚当たり数個以下であった。

第4図は、本実施例および従来のディップ式洗浄装置を用いた場合の、少数キャリアの再結合ライフタイムの測定結果を示す。

洗浄面を露出させた半導体基板を10分間処理した後、純水により10分間リンスを行なった。洗浄後の半導体基板を950℃の酸化性雰囲気中で熱処理した後、少数キャリアの再結合ライフタイムを測定した。本実施例の洗浄装置によって処理を行なった場合と比較して、従来の洗浄装置によって処理を行なった場合は、少数キャリアの再結合ライフタイムはいずれも低下している。

少数キャリアの再結合ライフタイムは半導体基板表面の汚染と密接な関係があり、汚染量が多いと再結合ライフタイムは低下する。このことから、本実施例の洗浄装置によって処理された半導体基板表面は、従来の洗浄装置によって処理された場合よりも、清浄であるといえる。

〔発明の効果〕

以上説明したように本発明は半導体基板の洗浄装置に、アンモニアまたは塩酸または硝酸の蒸気を発生する蒸気発生部と、発生した蒸気中にオゾン・ガスを導入するガス導入部とを具備することによって、半導体基板表面への微粒子の付着を防ぐことができる上に、半導体基板表面への不純物の汚染も防止することができる。さらに、蒸気を利用することにより、細部に至るまで均一に処理することができる。従って、より高品質、高歩留の半導体装置を製造することができる効果がある。

図面の簡単な説明

第1図および第2図は本発明の第1および第2の実施例の模式断面図、第3図は本実施例および従来の洗浄装置を用いた場合の、半導体基板表面に付着する微粒子の測定結果を示す図、第4図は本実施例および従来の洗浄装置を用いた場合の、少数キャリアの再結合ライフタイムの測定結果を示す図である。

1…処理槽、2…アンモニア溶液、3…ヒーター、4…蒸気発生部、5…オゾン・ガス導入管、6…オゾン発生器、7,7A,7B…フィルター、8…ガス導入部、9…半導体基板、10…キャリア、11…冷却器、21…水蒸気発生器、22…蒸気発生器、23…ガス供給装置、24…酸素ガス供給装置、25…紫外線光源。

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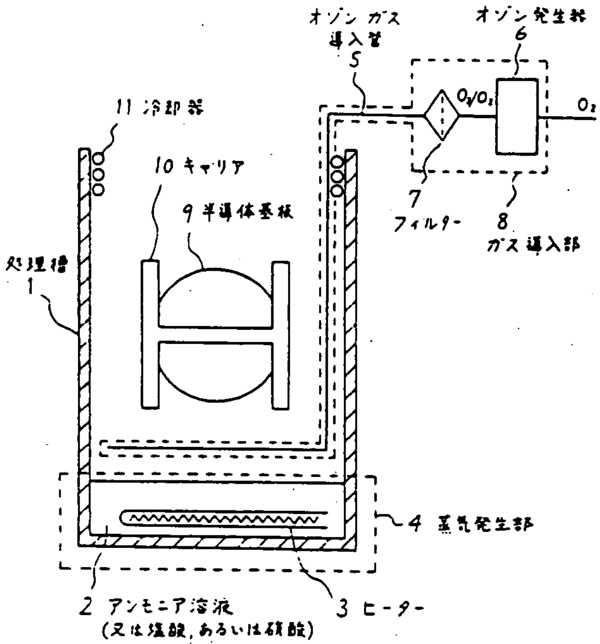
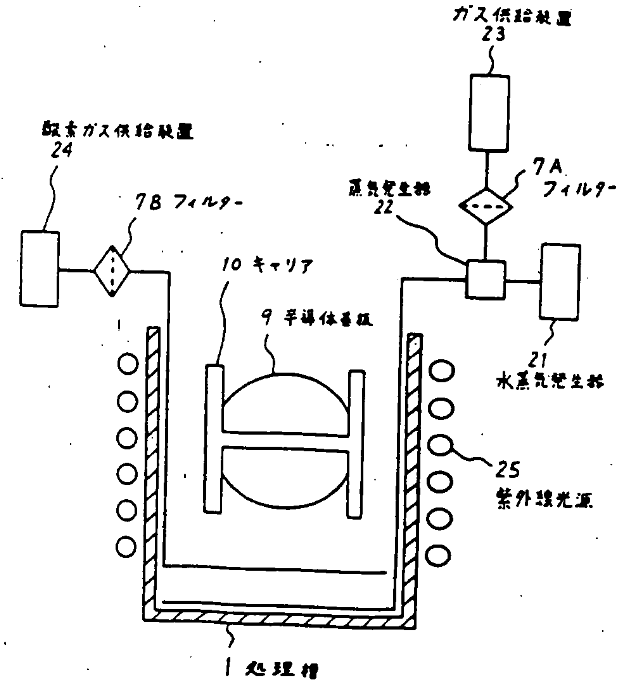
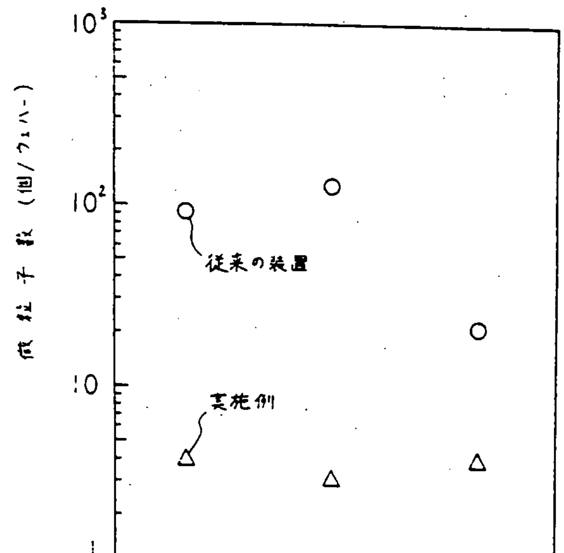



第 1 図

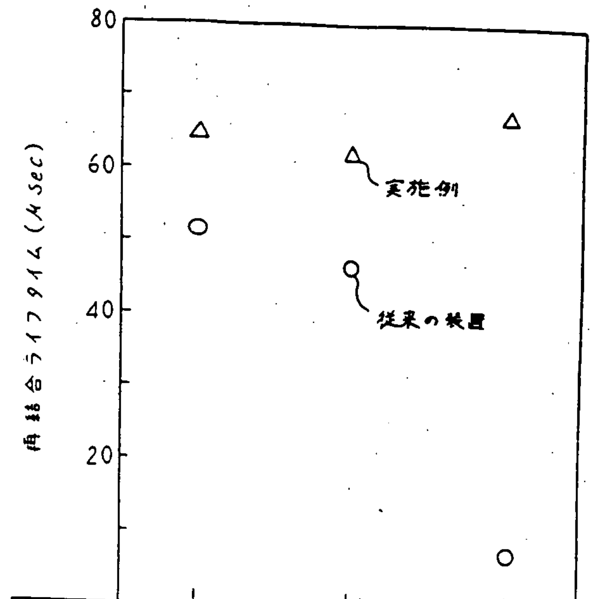



第 2 図




| | | | |
|---|---|---|---|
| 実施例 | $HCl$ 蒸気 / $O_3$ | $HNO_3$ 蒸気 / $O_3$ | $NH_4OH$ 蒸気 / $O_3$ |
| 従来の装置 | $HCl/H_2O_2/H_2O$ | $HNO_3/H_2O_2$ | $NH_4OH/H_2O_2/H_2O$ |

第 3 図




| | | | |
|---|---|---|---|
| 実施例 | $HCl$ 蒸気 / $O_3$ | $HNO_3$ 蒸気 / $O_3$ | $NH_4OH$ 蒸気 / $O_3$ |
| 従来装置 | $HCl/H_2O_2/H_2O$ | $HNO_3/H_2O_2$ | $NH_4OH/H_2O_2/H_2O$ |

第 4 図

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(54) Name of Invention: Cleaning Device for Semiconductor Substrate
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## Specifications

Name of Invention

Cleaning Device for Semiconductor Substrate

Claims

A cleaning device for a semiconductor substrate is characterized by the fact that it is equipped with the following: a steam generator which is used to generate steam comprised of ammonia ($NH_4OH$), hydrochloric acid ($HC\ell$), or nitric acid ($HNO_3$); and a gas introduction device which is used to introduce ozone ($O_3$) gas into the steam that is generated by the aforementioned steam generator.

Detailed Description of the Invention

<Industrial Field of Application>

This invention pertains to a cleaning device for semiconductor substrates.

<Prior Art>

Previous examples of this type of cleaning device are mainly those referred to as dip-type devices in which the semiconductor substrates are dipped into a cleaning liquid in order to be treated. Other examples include spray-type devices in which cleaning liquid is sprayed in the form of a mist onto a rotating semiconductor substrate, as well as spin-type devices in which the cleaning liquid is applied to the semiconductor substrate through a spinning action.

<Problem to be Solved by the Invention>

In the case of the dip-type devices noted above, the semiconductor substrates are directly immersed within the cleaning liquid during treatment, and for this reason, if any minute impurities exist within the cleaning liquid, their particles will adhere to the surface of the semiconductor substrates. Therefore, a circulating filter device is indispensable for the sake of removing minute particles from within the treatment tank during the cleaning operation. However, this type of circulating filter device cannot completely prevent minute particles from adhering to the semiconductor substrates, and these particles will accumulate within the cleaning liquid as treatments are conducted over time. Furthermore, in cases where the cleaning liquid becomes contaminated for any reason, any semiconductor substrates that are treated in this liquid will also be completely contaminated.

On the other hand, in the cases of the spray-type and spin-type cleaning devices, since the cleaning liquid is used up for each batch, the benefit is that there will be few cases in which minute particles will re-adhere themselves to the surfaces of the semiconductor substrates due to accumulation. That being said, the fact that the cleaning liquid still makes direct contact with the semiconductor substrates causes the same type of contamination problem as in the case of the dip-type if treatments are conducted using contaminated cleaning liquid.

Minute particles and contaminants that adhere to the surfaces of semiconductor substrates during the cleaning process will have an adverse effect on each of the semiconductor manufacturing processes that follow, namely the diffusion/oxidation process, lithography process, etc. For example, this could cause abnormal diffusion during the diffusion/oxidation process, non-uniformity of the oxidation film thickness, etc., which could give rise to crystal defects. This may also lead to pattern defects during the lithography process. As a result, the semiconductor device properties may become deteriorated, which could cause a drop in production yields and lead to a reduction in quality.

In the cases of the prior spray-type and spin-type cleaning devices, the fact that the cleaning liquid is completely used up results in an increase in the amount of chemicals that are used when compared to the dip-type devices.

In the cases of the dip-type, spray-type and spin-type devices, hydrogen peroxide is used as an oxidizing agent. However, a breakdown of the hydrogen peroxide within the cleaning liquid may cause it to deteriorate, making it impossible to maintain a high level of cleaning strength over an extended period of time. Furthermore, due to the bubbles that are generated when hydrogen peroxide breaks down, the cleaning liquid is prevented from reaching the most detailed portions of the semiconductor substrates. In particular, with the increase in the level of integration within semiconductor devices in recent years, there is a trend toward an increase in the aspect ratio, which means that there is an even greater demand for the ability to conduct reliable cleaning operations given a high aspect ratio.

In order to prevent the deterioration of the cleaning liquid, there is a method in which ozone gas ($O_3$) is used in place of hydrogen peroxide. However, the problem with this method in the case of prior cleaning devices is that it easily results in a non-uniform cleaning effect due to the fact that the $O_3$ is delivered within the cleaning liquid through the use of a bubbling technique.

<Means for Solving the Problem>

The cleaning device for semiconductor substrates that is described in this invention is equipped with a steam generator which is used to generate steam comprised of ammonia, hydrochloric acid, or nitric acid as well as a gas introduction device which is used to introduce ozone gas into the steam that is generated.

<Embodiments>

The following are embodiments of this invention in which drawings are used for reference.

Figure 1 is a cross-sectional model diagram of a cleaning device that represents the No. 1 embodiment of this invention.

In Figure 1, an ammonia solution 2 (or a solution comprised of hydrochloric acid or nitric acid) is delivered into the bottom of the treatment tank 1. Heating this ammonia solution 2 using a heater 3 generates an ammonia steam. In this case, the steam generator 4 is comprised of the heater 3. An ozone gas introduction tube 5 is used to introduce ozone gas into the ammonia steam that has been generated. The ozone is produced when a portion of the oxygen gas ($O_2$) that is delivered to the ozone generator 6 is converted into ozone within said generator. This creates a mixed gas of ozone/oxygen ($O_3$/ $O_2$), which is introduced after it passes through the filter 7. In this case, the gas introduction portion 8 is comprised of the ozone generator 6, the filter 7, and the ozone gas introduction tube 5.

In this fashion, the semiconductor substrate 9 is exposed and treated within the ammonia steam in which ozone gas has been introduced. The semiconductor substrate 9 is supported through the use of a carrier 10. After the ammonia steam is liquefied using a cooler 11, it is returned to the treatment tank where it is reused.

Thus, in this embodiment, the use of ammonia as a steam makes it possible to prevent minute particles or contaminants from adhering to the surface of a semiconductor substrate even in the case where these substances may have existed within the original chemicals. Furthermore, it becomes possible to clean even the most detailed portions of the semiconductor substrate.

According to this No. 1 Embodiment, an immersion heater is used to heat the cleaning liquid, but it is also acceptable to use a method in which heating is conducted from the outside of the treatment tank. It is also possible to use another type of heating method such as infrared heating or lamp heating. In addition, the No. 1 Embodiment explains a case in which ammonia is used, but it is also possible to conduct exactly the same type of cleaning using hydrochloric acid or nitric acid.

Figure 2 is a cross-sectional model diagram of a cleaning device that represents the No. 2 embodiment of this invention.

According to this No. 2 Embodiment, the ammonia steam is obtained by allowing ammonia gas to make contact with water steam. In the cases of nitric acid steam and hydrochloric acid steam, nitrogen dioxide and hydrogen chloride gas are used, respectively. The water steam that has been created through the use of the steam generator 21 is sent to another steam generator 22, where the water steam absorbs the ammonia gas that has passed through the filter 7A from the ammonia gas ($NH_3$) delivery device 23, resulting in the generation of ammonia steam. This ammonia steam is then introduced into the treatment tank 1.

At the same time, oxygen gas passes through the filter 7B from the oxygen gas delivery device 24 and is introduced into the treatment tank 1. At this point, ultraviolet light is irradiated from an ultraviolet light source 25 that is installed onto the side of the treatment tank 1. Through the action of this ultraviolet light, the oxygen gas is converted into ozone. As such, the semiconductor substrate 9 undergoes treatment within an atmosphere in which ammonia steam is mixed with ozone. Although a carrier 10 is used to support the semiconductor substrate 9 in the case of this No. 2 Embodiment as well, it is also possible, of course, to conduct a single-wafer treatment process.

Figure 3 shows the measurement results for this embodiment as well as a prior dip-type cleaning device with regard to the minute particles that adhere to the surface of a semiconductor substrate in each case.

After a 10-minute treatment process is conducted on a number of semiconductor substrates using a prior device as well as this embodiment, the substrates are rinsed for 10 minutes using purified water. The substrates are then dried, and measurements are taken in order to determine the number of minute particles that have adhered to each substrate. In the case of the process that was conducted using the prior device, the number of particles per substrate was approximately 100 with regard to $HC\ell/H_2O_2/H_2O$ and $HNO_3/H_2O_2$, and with regard to $NH_4OH/H_2O_2/H_2O$, the number was approximately 20. In comparison, the process conducted using the cleaning device described in this embodiment resulted in no more than a few particles per substrate in either case.

Figure 4 shows the recombination lifetime results for the minority carriers in the case where this embodiment is used as well as a prior dip-type cleaning device.

After a 10-minute treatment process is conducted for semiconductor substrates in which the cleaning surfaces have been exposed, the substrates are rinsed for 10 minutes using purified water. The cleaned semiconductor substrates are then heat treated in an oxidizing atmosphere at a temperature of 950°C, after which the recombination lifetime results for the minority carriers are measured. Compared to the case in which the treatment was conducted using the cleaning device described in this embodiment, the results for the case in which the prior device was used shows a drop in the recombination lifetime for the minority carriers in all cases.

The recombination lifetime for the minority carriers has a close relationship with the contamination of the surfaces of the semiconductor substrates, such that when there is a high level of contamination, a drop occurs in the recombination lifetime. Based on this, it can be said that the surfaces of the semiconductor substrates that were treated using the cleaning device described in this embodiment are cleaner than those that were treated using the prior cleaning device.

<Effect of the Invention>

As explained above, through the use of this invention in which a cleaning device for semiconductor substrates is equipped with a steam generator which is used to generate steam comprised of ammonia, hydrochloric acid, or nitric acid as well as a gas introduction device which is used to introduce ozone gas into the steam that has been generated, not only is it possible to prevent minute particles from adhering to the surface of a semiconductor substrate, but it is also possible to prevent contamination from impurities along the surface of a semiconductor substrate. Moreover, by using steam in this treatment process, it becomes possible to conduct a uniform treatment process even along the most detailed portions of a semiconductor substrate. Accordingly, the effect of this invention makes it possible to produce semiconductor devices at higher yields with an improved level of quality.

Simple Explanation of the Drawings

Figures 1 and 2 are cross-sectional model diagrams of cleaning devices that represent the No. 1 and No. 2 embodiments of this invention. Figure 3 shows the measurement results for this embodiment as well as a prior cleaning device with regard to the minute particles that adhere to the surface of a semiconductor substrate in each case. Figure 4 shows the recombination lifetime results for the minority carriers in the case where this embodiment is used as well as a prior cleaning device.

1: Treatment tank

2: Ammonia solution

3: Heater

4: Steam generator

5: Ozone gas introduction tube

6: Ozone generator

7, 7A, 7B: Filters

8: Gas introduction portion

9: Semiconductor substrate

10: Carrier

11: Cooler

21: Water steam generator

22: Steam generator

23: Gas delivery device

24: Oxygen gas delivery device

25: Ultraviolet light source

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Figure 1

5: Ozone gas introduction tube

6: Ozone generator

11: Cooler

10: Carrier

9: Semiconductor substrate

7: Filter

8: Gas introduction portion

1: Treatment tank

4: Steam generator

2: Ammonia solution

(Or hydrochloric acid, or nitric acid)

3: Heater

Figure 2

23: Gas delivery device

24: Oxygen gas delivery device

7B: Filter

22: Steam generator

7A: Filter

10: Carrier

9: Semiconductor substrate

21: Water steam generator

25: Ultraviolet light source

1: Treatment tank

Figure 3

[y-axis:] No. of Minute Particles (Number/Wafer)

[inside graph:]

Prior device

Embodiment

| | | | |
|---|---|---|---|
| Embodiment | $HC\ell$ Steam/$O_3$ | $HNO_3$ Steam/$O_3$ | $NH_4OH$ Steam/$O_3$ |
| Prior Device | $HC\ell/H_2O_2/H_2O$ | $HNO_3/H_2O_2$ | $NH_4OH/H_2O_2/H_2O$ |

Figure 4

[y-axis:] Recombination Lifetime (μ sec)

[inside graph:]

Embodiment

Prior device

| | | | |
|---|---|---|---|
| Embodiment | $HC\ell$ Steam/$O_3$ | $HNO_3$ Steam/$O_3$ | $NH_4OH$ Steam/$O_3$ |
| Prior Device | $HC\ell/H_2O_2/H_2O$ | $HNO_3/H_2O_2$ | $NH_4OH/H_2O_2/H_2O$ |